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13. ABSTRACT *(Maximum 200 words)*

The goal of this project was to develop an ion spectrometer capable of making absorption measurements on ions using cavity ring-down spectroscopy (CRDS). As part of our continuing goal of detecting ion products from ion-molecule reactions, we have successfully used CRDS to measure the vibronic absorption spectra of various small ions and radicals generated by a pulsed discharge nozzle. These spectra give information about the number densities and temperatures of the ions and radicals. Currently, our setup consists of a pulsed discharge nozzle that produces high concentrations of radicals and ions arranged perpendicular to the optical cavity made from two highly reflective mirrors. To date, we have obtained the absorption spectrum of N_2^+ and CN as well as several atomic species.

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1. INTRODUCTION

Ion-molecule reactions under nonthermal conditions continue to be of major importance in many Air Force applications, such as the low altitude orbiting and the atmospheric re-entry of satellites. One continuing objective of our work (AFOSR grant # F49620-01-1-0019) is the development of an ion spectrometer to measure the internal state distributions of product ions of hyperthermal ion-molecule reactions. Currently, our setup consists of a pulsed discharge nozzle that produces radicals and ions with a number density of at least 10^{13} cm^{-3}. At the expansion region, the ions will be allowed to react with other neutral reagents, and the resulting ion products will be detected using cavity ring-down spectroscopy (CRDS). Using the CRDS technique, we can directly measure the population of individual quantum states of the product ions.

CRDS is a sensitive laser-based spectroscopic technique capable of providing direct measurement of absolute absorption coefficients. Measurement of absorption coefficients in conjunction with the measured ion density, gives the absolute absorption cross section of the ionic species. Similarly, if the absorption cross section is known, the cavity ring-down signal can be used to determine the number of ions in a specific internal state. CRDS was first demonstrated by O'Keefe and Deacon in 1988[1] who employed a pulsed laser source. In CRDS, a laser pulse is coupled into a nonconfocal optical cavity formed by two high reflectivity mirrors. The intensity of the light pulse successfully coupled within the cavity decays exponentially owing to transmission and scattering losses by the cavity mirrors and absorption and scattering losses by gas phase species present within the cavity. The exponentially decaying intensity of the trapped laser pulse is monitored by detecting the small fraction of light transmitted by the output mirror. By measuring this decay rate as a function of laser frequency, the absorption spectrum of species present within the cavity is obtained.

The inherent sensitivity of the CRDS technique stems from the fact that the decay rate is insensitive to fluctuations in the intensity of the laser source, fluctuations that limit the sensitivity of other direct absorption techniques. The advantage of CRDS over other

sensitive absorption techniques, such as photoacoustic spectroscopy and frequency modulation spectroscopy, is the ability of CRDS to directly measure absolute concentrations of gas-phase species. To date, CRDS employing pulsed lasers has been successfully applied when the loss from absorption was as little as 7×10^{-10} cm^{-1},[2] while CRDS systems employing continuous wave (CW) laser sources have detected absorption losses as low as 6×10^{-11} cm^{-1} with a 1 s integration period.[3] This technique has been applied to measure the temperature of OH radicals in flames,[4,5,6] the spectrum of N$_2^+$ in the ultra-violet,[7] and linear carbon chain radicals and ions in the visible.[8]

One of the main difficulties in studying ion-molecule reactions using absorption techniques is the maintenance of the high ion densities. Owing to their own reactivity, ions are rapidly depleted after generation. Recent advances in ion storage techniques, namely ion traps, have made it possible to store and guide ion beams with densities as high as 10^8 cm^{-3}.[9] However, this density is not yet high enough for optical detection schemes using absorption. Moreover, the storage volume is usually very small, making the experiments more difficult. Normally, high concentrations of ions are generated using discharges like hollow cathodes or plasma torches. In spite of high yields, ions from these sorts of discharge sources usually have extremely high rotational and vibrational temperatures, imposing complications on spectroscopic detection. However, it was reported that the internal temperature of the ions could be lowered substantially if the discharge is combined with a supersonic expansion from a nozzle.[8,10] In our laboratory, a new apparatus was constructed to accommodate such a discharge nozzle where ions with a number density of 10^{13} cm^{-3} can be generated with relative ease.

2. Detection of Ions and Radicals using CRDS

As an intermediate step of our ultimate goal of detecting ion products from ion-molecule reactions, an ion absorption spectrometer has been constructed with the purpose of measuring the vibronic absorption spectra of various small ions and radicals. The schematic of the pulsed discharge nozzle is shown in Figure 1. Discharge electrodes are

attached on top of a pulse nozzle (General Valve). Electrical shielding from the nozzle body is achieved by inserting an insulator plate made of delrin between the nozzle and the electrodes. The electrode closer to the nozzle body is electrically grounded while the one further downstream from the nozzle is attached to a negative high voltage supply through an adjustable ballast resistor. The voltage and the resistance are tuned to obtain the most stable discharge condition. The discharge starts and ceases automatically with gas flow through the aperture. Unlike the previous report, there has been no arching to the grounded chamber walls.[11] Typically, the discharge works with a 400 V difference between the electrodes with about 2 A of current.
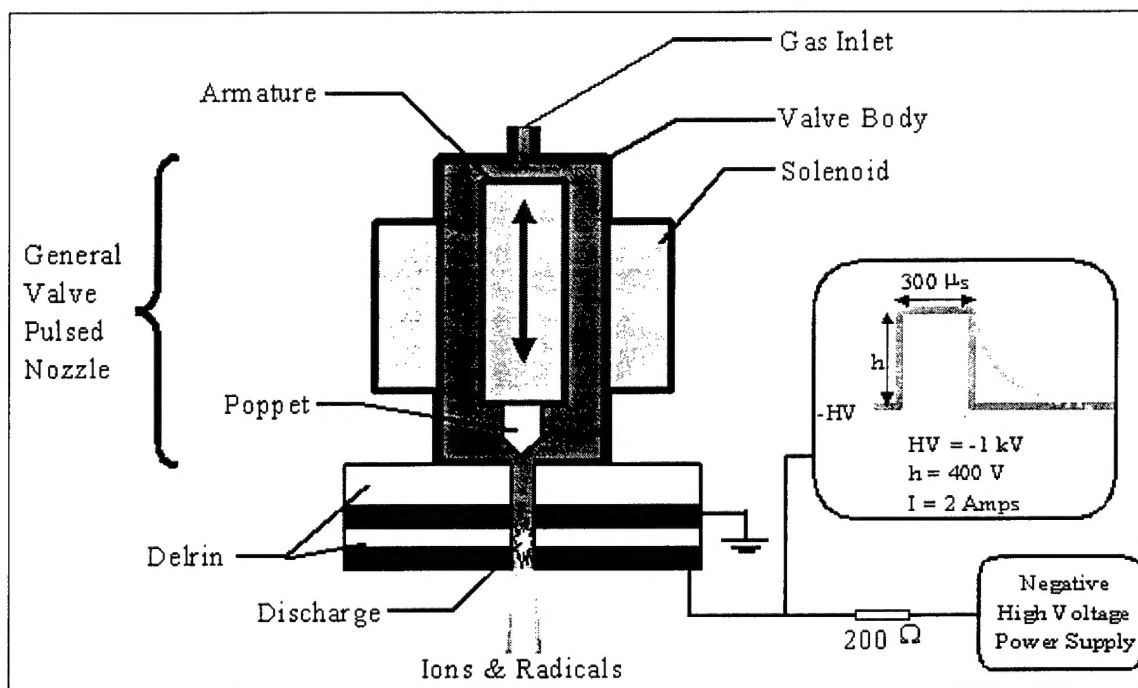

Figure 1. Schematic diagram of the pulsed discharge nozzle

Figure 2 shows a schematic of the CRDS apparatus. A Nd:YAG pumped dye laser (PDL3, Spectra Physics) is used to generate light between 387 and 392 nm for measuring N_2^+ and between 386 and 389 nm for measuring the CN radical. Pulses of light from the dye laser are coupled into the optical cavity, which is 0.8 m in length and comprised of two high reflectivity mirrors (Los Gatos Research, R = 0.9997 at 390 nm) set up

perpendicular to the gas expansion axis. A photomultiplier tube (PMT) (Hamamatsu R955) measures the leakage of light through the output mirror. Photocurrent from the PMT is digitized using a digital oscilloscope (Hewlett-Packard 54510A) and a personal computer is used to fit the decay waveforms to an exponential function and exact the ring-down time τ, while stepping the dye laser through the wavelength range of interest. The discharge nozzle is mounted on a translatable flange allowing the discharge to be moved in each Cartesian coordinate.
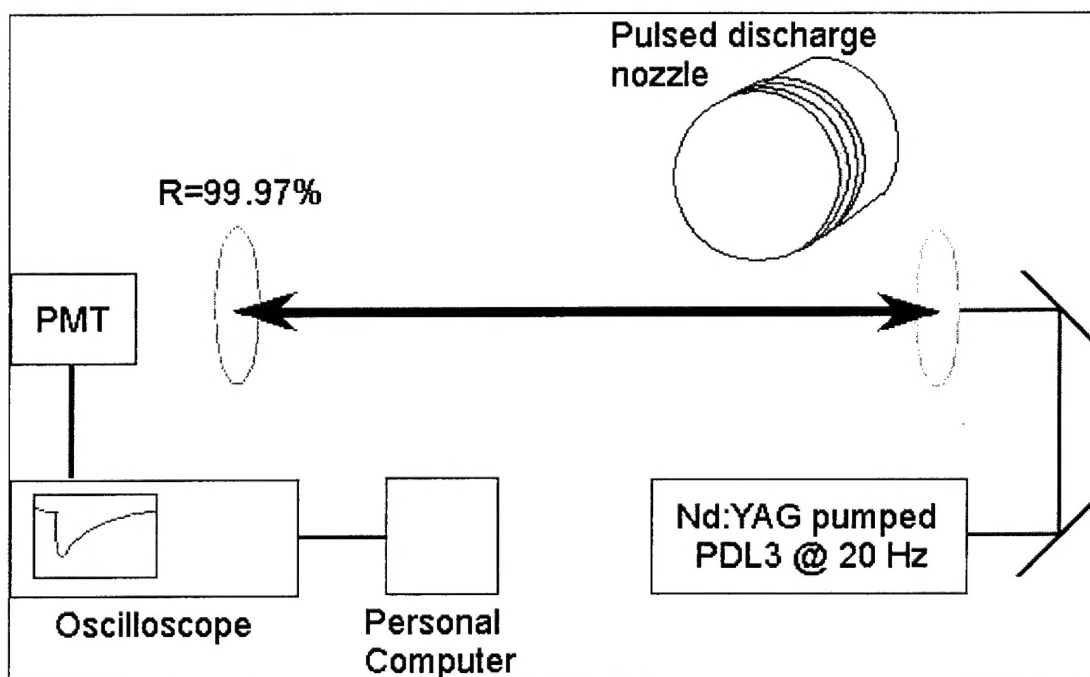

Figure 2. Schematic diagram of CRDS setup

To date, the $X^2\Sigma_g^+ \rightarrow B^2\Sigma_u^+$ transition of N_2^+, the $X^2\Sigma^+ \rightarrow B^2\Sigma^+$ of CN and several atomic transitions have been recorded. The CRDS spectrum of N_2^+ is shown in Figure 3. Pure N_2 at a backing pressure of 2 atm was expanded through the discharge plates into the vacuum chamber with a background pressure of ~1.4 x 10^{-4} torr. The line of sight lies

1 cm away from the electrode assembly, leading to the reduction in ion concentration by a factor of 100 compared to the concentration at the expansion orifice. The spectrum shown in Figure 3 corresponds to a concentration of N_2^+ on the order of 10^{11} cm^{-3} at a temperature of about 330 K. A similar spectrum has been obtained by probing the $X^2\Sigma^+ \rightarrow B^2\Sigma^+$ transition of the CN radical from the discharge of 5% CH_3CN seeded in Ar (Figure 4). We estimate that the number density in the probe region for the CN spectrum was on the order of 10^{10} cm^{-3}.
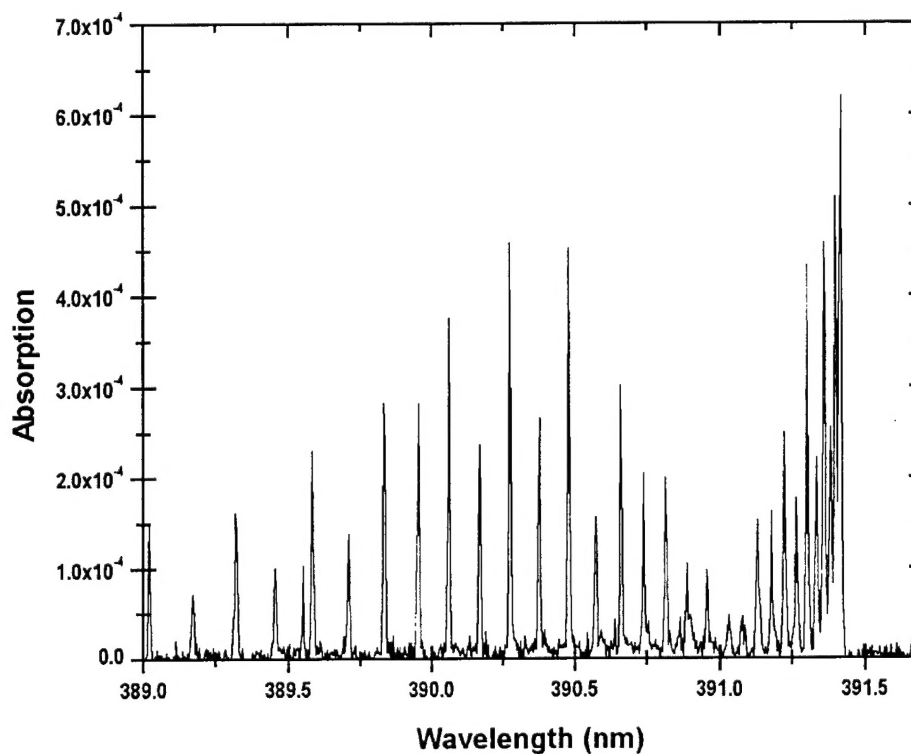

Figure 3. The $X^2\Sigma_g^+ \rightarrow B^2\Sigma_u^+$ transition of N_2^+
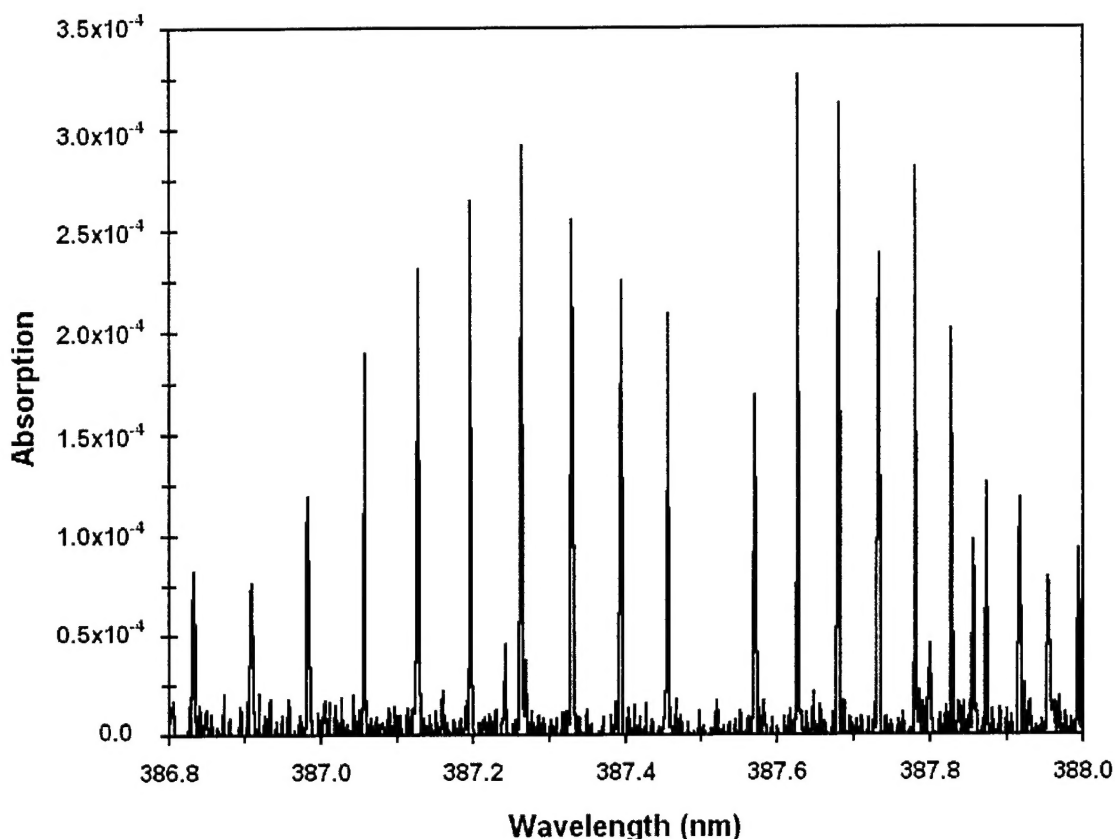
Figure 4. The $X^2\Sigma^+ \rightarrow B^2\Sigma^+$ transition of CN

Several improvements to the current setup are currently in progress. The data taken above used a Quanta-Ray PDL-3 dye laser with a linewidth of about 0.07 cm^{-1}. That laser has been replaced by a Lambda Physik Scanmate 2E dye laser that offers a linewidth of 0.03 cm^{-1}. The decrease in bandwidth increases the sensitivity of the spectrometer because the ring-down decay more closely resembles a single exponential decay when the linewidth of the absorption feature is broader than the linewidth of the light inside of the cavity.[12] Although the absorption feature of a gas in a supersonic discharge is still smaller than the linewidth of the new dye laser, some improvement should be realized because a greater proportion of the light will be on resonance with the transition of interest. A second improvement to the spectrometer is the construction of a slit discharge nozzle instead of the pinhole discharge nozzle used to collect the data above. A slit nozzle offers two benefits over a pinhole, an increased pathlength of the

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absorbing sample and the number density falls as 1/r for a slit nozzle compared to $1/r^2$ for a pinhole. Because the pulsed nozzle can be translated, spatially resolved concentration and temperature profiles of ions produced by the pulsed discharge nozzle will also be measured allowing a greater understanding of the discharge process in a supersonic expansion. The present DURIP grant has allowed us to augment our instrumentation in a significant manner, which we hope will allow improved cavity ring-down spectra of ions and radicals.

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APPENDIX A: EQUIPMENT REPORT
03/01/01-02/28/02

Item	Cost
Powerlite Precision II 8020 Q-switched Nd:YAG laser with injection seeder, power supply and harmonic generators	$79,480.00
Toshiba laptop computer with I-Omega zip drive	1,828.00
Windows DLL kit	378.00
Dell Dimension L computer	947.16
355nm Laser mirrors and high energy harmonic separator	1,312.20
Bertan high voltage power supply	3,086.00
Standard dye circulator and filters for main amplifier	5,162.00
MCP detector with mounting flange, voltage divider, and cable set	10,500.00
TE-300 and associated equipment	13,999.44
VT120C fast timing preamplifier	432.00
Silicon avalanche photodioedes	10,972.50
Dell dimension computer	1,631.80
Taxes and shipping charges on equipment	21,112.90
TOTAL	**$150,842.00**